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#### 7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Good progress has been made in all three areas of work supported by the Contract.

A. Improvement and Extension of Current Procedures. Our AMPAC computer program has been extensively rewritten. The new version runs 2-3 times faster on scalar computers and is also easily vectorizable. The improvement on vector computers should therefore be still greater. Studies of reactions have been facilitated by a new procedure for finding transition states. CI calculations have been greatly accelerated by development of analytical derivatives.

MNDO has been parametrized for additional elements (zinc, mercury, germanium, and lead) and reparametrized for silicon. AM1 has been parametrized for boron, silicon, germanium, zinc, and mercury. However, our most important contribution has been the discovery of AM1 parameters for phosphorus and sulfur that give good results for compounds in all their valence states, including  $P^V$ ,  $S^{IV}$ , and  $S^{VI}$ . The results should be of major value in biochemistry, medicinal chemistry, etc.

B. New Procedures. While MNDO and AM1 have proved very effective, we have at last had to accept that they cannot be extended to transition metals because the MNDO/AM1 formalism cannot be applied to d AOs. We have therefore begun work on a new "third generation" treatment where this problem will not arise. Writing the necessary computer programs proved a massive undertaking. Parametrization is in progress.

Biradicals represent another unfortunate weakness of MNDO and AM1. We are currently parametrizing a version of AM1 with CI included throughout (cf Thiel's MNDOC) which should solve this problem.

**C. Applications to Chemical Problems.** Extensive studies of pericyclic reactions (Diels-Alder reaction, Cope and Claisen rearrangements, ene reactions, dipolar additions) have led to major revisions of generally accepted ideas concerning their mechanisms (Woodward-Hoffmann rules). A further very important result was the discovery that reactions may take place by different paths that differ only in the detailed geometries of the corresponding transition states (TS). This enormously increases the amount of computation needed to establish the mechanism of a reaction because it can no longer be assumed that finding a TS implies that there are no others. The others must be found and located, or, harder still, it must be shown no such alternative exists. Our work on the Cope rearrangement also showed that correlated *ab initio* methods, using very large basis sets, are needed to arrive at reliable conclusions.

Model calculations for two enzyme reactions (conversion of farnesyl pyrophosphate to squalene and the chain extension step in the biosynthesis of fatty acids) supported our interpretation of the efficiency and selectivity of enzymes as catalysts in terms of the exclusion of water from between them when the substrate is adsorbed in the active site.

*Ab initio* calculations for the [1,5]sigmatropic hydrogen shift in 1,3-pentadiene supported our suggestion that the reaction involves tunnelling from vibrationally excited states (Vibrationally Excited Tunnelling, VAT).

An investigation of the rearrangement of azulene to naphthalene, and the automerization of naphthalene, involved the location of 89 (!) stationary points on the  $C_{10}H_8$  potential surface, most of them requiring the use of open shell procedures. This is unquestionably the most complex system ever studied by any quantitative quantum mechanical procedure. It led to novel mechanisms which seem to have been accepted.

A wholly novel "chemical" mechanism has been suggested for the superconductivity of the new high temperature superconductors. It is the only one so far proposed that is consistent with *all* the available data.

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FINAL SCIENTIFIC REPORT

October 1, 1985 to November 1, 1988

Contract AFOSR-86-0022

Development of Practical MO Techniques for Prediction of

The Properties and Behaviour of Materials

Michael J. S. Dewar, The University of Texas, Austin, Texas 78712

1. INTRODUCTION

The work supported by this Contract has been very productive, both in the improvement and extension of our theoretical procedures and in applications of them to specific chemical problems. Indeed, my main problem is a large back log of papers to write; 18 MSS are in various stages of preparation.

The most notable advances in computational procedures include the development of seemingly satisfactory AM1 parameters for phosphorus and sulfur that apply to all their valence states, analytical derivatives for treatments including CI which allow such calculations to be carried out at reasonable expense, and a new and very effective procedure for locating transition states. AM1 parameters for boron and silicon also provide much better results than earlier MNDO treatments. Work has also begun on two new semiempirical treatments in the hope of overcoming the unsatisfactory treatment of biradicals by AM1 and the failure of attempts to introduce d-orbitals into it.

As regards applications; studies of a number of reactions have shown that AM1 represents a major advance over other semiempirical treatments for the study of reaction mechanisms. Our most important contribution in this area has been a revision of current ideas concerning the mechanisms of pericyclic reactions, derived from very extensive studies of a number of different examples. An extensive survey of elimination reactions also seems to have provided definitive information concerning their mechanisms. Calculations for a number of other reactions have also led to novel and significant mechanistic conclusions.

A novel possible mechanism for superconductivity has also been suggested which seems to account for the properties of the recently discovered high temperature superconductors.

These and our other contributions are treated in more detail below. Only completed projects are reviewed. The references are to the numbered list of publications arising from the Contract.

## 2. THEORETICAL PROCEDURES

### 2.1 Extension of MNDO and AM1 to Additional Elements.

(a) Second Period Elements. AM1 parameters have been developed for the halogens (41) and boron (36). The results for boron compounds represent a major improvement over MNDO and indeed over all but "state of the art" *ab initio* procedures. Thus AM1 reproduces the pyramidal geometries of pentaborane and other analogous boron hydrides, a feat previously achieved only by very high level *ab initio* methods, and it gives good estimates of the activation energies for hydroboration



reactions, for which the MNDO values had been too large. The halogen parameters also lead to results that are generally superior to those given by MNDO.

(b) Phosphorus and Sulfur. One of the major omissions in our treatments has been the lack of satisfactory parameters for phosphorus and sulfur. This has greatly restricted their applications to biological systems. In spite of much effort, we had been unable to obtain MNDO or AM1 parameters that could simultaneously account for the properties of compounds containing P or S in their higher valence states as well as their normal states ( $P^{III}$ ,  $S^{II}$ ). While an improved set of parameters were obtained (15) for  $S^{II}$ , the errors for compounds containing  $P^V$ ,  $S^{IV}$ , or  $S^{VI}$  were still very large ( $>100$  kcal/mol). While the failure was attributed to the omission of d AOs and/or to neglect of the changes in the properties of AOs with atomic charge, we have now found that it was in fact due to our having been trapped in "wrong" minima on the parameter hypersurfaces. We now have AM1 parameters for phosphorus (49) and sulfur (52) that reproduce the properties of *all* their compounds in an apparently satisfactory manner.

(c) Silicon. While an "improved" set of MNDO parameters for silicon was developed (13) during the current contract period, this was later found to suffer from a number of quite serious deficiencies. The problems seem to have been overcome by a recent parametrization of silicon in AM1 (26).

(d) Zinc. Parameters for zinc were developed, both in MNDO (16) and in AM1 (37). While the results are subject to more uncertainty than usual, due to the dearth of thermochemical data for zinc compounds, applications suggest that the AM1 parameters in particular lead to satisfactory results. This should prove a useful contribution in view of the importance of zinc in biochemistry.

(e) Other Elements. MNDO parameters have been reported for mercury (6), lead (8), and germanium (23). AM1 parameters have also been developed for germanium (53) and mercury (54). The test calculations reported in the papers describing the parameters seem to suggest that AM1 will prove generally superior to the previous MNDO treatment.

## 2.2 Technical Improvements in AMPAC.

(a) Calculations Including CI. Our previous work had shown that open shell systems are best treated by a version of the "half-electron" method where 3x3 CI was included. In our AMPAC program, this is the default procedure for radicals, while in the case of biradicals it corresponds to the BIRADICAL option. Use of this approach has, however, been restricted by the amount of computer time it needs. Most studies of open shell systems and biradicals have therefore been carried out using the inferior UHF approach. The problem lay in the evaluation of analytical derivatives of the energy, needed for geometry optimization. These had to be found by finite difference using full SCF calculations. The difficulty has now been overcome by development of analytical expressions for the derivatives (48). These are moreover found by a new procedure which is much faster than existing ones in cases where, as here, only limited CI is included.

RHF AM1 (or MNDO) calculations for open shell systems now take little longer than those for analogous closed shell ones.

(b) Location of Transition States. Our standard procedure in studying reactions has been to use the reaction coordinate method to locate the transition states and then to refine their geometries by the McIver--Komornicki method. When this approach works, it is as good as any, but unfortunately it often fails. In the past we were forced to resort to expensive two-dimensional grid searches. A solution seemed to have been provided some years ago by a new procedure we developed for locating TSs. This, however, also frequently fails. When Dr. Daniel Liotard has now developed yet another new procedure (chain method) which seems to be totally reliable. While it needs a lot of computing time, it is the best alternative when the reaction coordinate method fails.

2.3 Revival of a  $\pi$  SCF Approximation (DEWARPI). Our early work on semiempirical procedures was confined to ones based on the  $\sigma, \pi$  approximation because the computers available then were too slow for all-valence-electron methods to be feasible. However, our final  $\pi$  SCF treatment proved remarkably effective, reproducing the heats of formation of conjugated and aromatic hydrocarbons as accurately as they can be measured. A new computer program (DEWARPI) for this procedure has been written and submitted to QCPE. A PC version has aroused much interest as a potential teaching aid.

## 2.4 New Procedures

(a) AM1C. Problems arise in attempts to carry out MINDO/3, MNDO or AM1 calculations for biradicals or biradical-like species if the "unpaired" electrons are so strongly correlated that open shell versions of MNDO or AM1 have to be used. Since the latter allow completely for the correlation between the two "unpaired" electrons and since an average allowance for correlation is included in these treatments via the parametrization, the energies found are too negative by the average pair correlation energy ( $\sim 1\text{eV}$ ).

While Thiel has provided a solution of this problem by parametrizing a version of MNDO with full CI included throughout, the resulting treatment (MNDOC) has proved of limited value because of the amount of computing time needed for geometry optimizations, due to the estimation of derivatives of the energy by finite difference. Since our development of analytical derivatives (2.2(a) above) has overcome this problem, we decided to develop an analogous version (AM1C) of AM1. All the necessary programs have been written and we have also established the level of CI necessary. Parametrization is now in progress.

(b) AM2. Three years ago we were finally forced to admit that  $d$  AOs cannot be included effectively in the MNDO/AM1 formalism. Work has therefore begun on a "fourth generation" semiempirical treatment (AM2) in which the repulsion integrals will be calculated theoretically and scaled by a function of distance to allow for correlation. The basic AM2 program has been written and included in our parametrization program. Time was wasted initially by attempts to use theoretical values for the core--electron attractions as well as for the electron-electron repulsions. This proved impracticable so we have reverted to the Goeppert-Meyer-Sklar

approximation, as in AM1. While parametrization is now in progress, progress has been slow because of inadequate computer facilities. We badly need additional CPU units for our Alliant computer. The first stages in the development of a new procedure of this kind are always very time consuming because they involve finding the best forms of functions, here the weighting factor function for the repulsion integrals and the core-core repulsion function. This can be done only by laborious trial-and-error. It is annoying to be handicapped in this work by problems with computation.

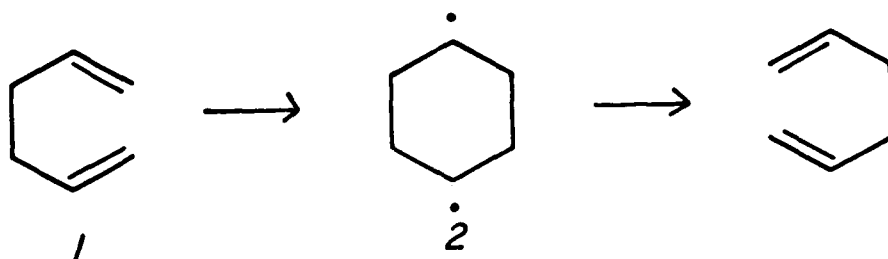
A surprising but encouraging result followed from comparisons of the theoretical values for the electron repulsion integrals with those given by MNDO or AM1. The latter were clearly too small at larger internuclear separations. Since the core-electron attractions in AM1 are set equal to *minus* the corresponding electron-electron repulsions, following the Goeppert-Meyer-Sklar formalism, and since there are two such attractions for each repulsion, the calculated total energy must be too *positive*. It seems likely that the apparent underestimation of repulsive interactions in MNDO is due to this. We therefore hope to be able to avoid the need for the inelegant gaussian core repulsion terms in AM2.

### 3 APPLICATIONS TO REACTIONS

#### 3.1 Pericyclic Reactions.

(a) The Cope Rearrangement. Some years ago we concluded on the basis of MINDO/3 calculations and experimental studies that the Cope rearrangement of 1,5-hexadiene (1) takes place in a nonsynchronous manner by the Doering biradicaloid mechanism, rather than by the synchronous

pericyclic mechanism predicted by the Woodward-Hoffmann rules. The symmetrical intermediate, instead of being aromatic, is a biradical-like species derived from the 1,5-cyclohexylene biradical (2).



Since this conclusion was recently challenged on the basis of *ab initio* calculations, we decided to reexamine the problem in detail, using AM1. Calculations were carried out (29) for the chair Cope rearrangements of 1 and for a number of its derivatives (2-phenyl, 3-phenyl, 2,4-diphenyl, 2,5-diphenyl, 3-methyl) for which experimental data were available. The results entirely confirmed the Doering mechanism, the calculated activation parameters, secondary deuterium kinetic isotope effects (SDKIE), and proportions of isomers in the products, all agreeing remarkably well with experiment.

However, one discrepancy remained. While the early MINDO/3 calculation had reproduced the enthalpies of activation for the boat and chair rearrangements of 1 very nicely, and also the entropy of activation for the chair rearrangement, the calculated entropy of activation for the

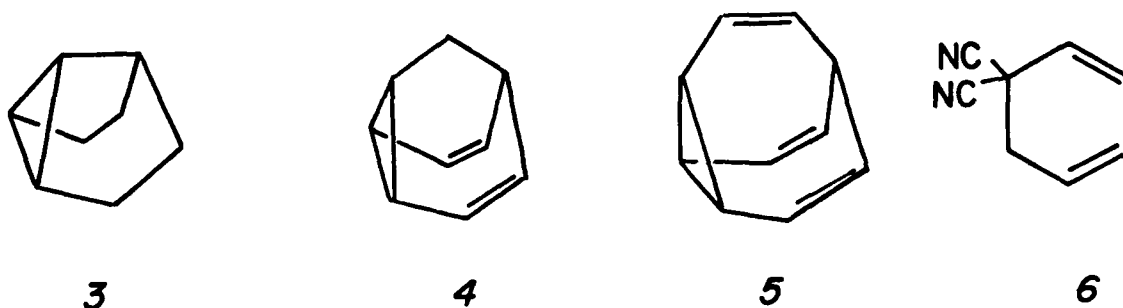
boat was too positive by 10 cal/deg. Furthermore, the AM1 calculations led to similar results. The discrepancy was too large to be reasonably attributed to experimental error or error in the calculations.

This problem was solved (32) by the discovery that each of these reactions can take place by two distinct paths, each with an apparently normal TS. One TS (ARO) had the structure expected for a typical "allowed" pericyclic reaction while the other corresponded to the biradicaloid (BR) involved in the Doering mechanism. The entropy of activation for the ARO path was in each case within the error limits of the experimental value for the boat Cope rearrangement of 1. Furthermore, while the BR path was predicted to have the lower free energy of activation in the case of the chair rearrangement the reverse was true for the boat.

This conclusion has far reaching consequences for chemical theory, quite apart from its significance concerning the mechanism of the Cope rearrangement. It has always been tacitly assumed that if a reaction leads from a given reactant to a given product in a single kinetic step, it can do so in only one way, via a unique TS. If then a TS is found for such a reaction, there is no need to look further because it must necessarily be the one and only TS.

Our results invalidate this assumption. A reaction can take place by more than one path, via one or other of two or more distinct TSs. If there are two or more possible TSs for a given reaction, no conclusions can be drawn concerning its mechanism until *all* possible TSs have been located or unless all but one of them have been shown not to exist.

This conclusion is disastrous from the *ab initio* point of view because it enormously increases the amount of calculation that has to be carried out in order to determine the mechanism of a reaction. The situation is indeed even worse than it seems because in many cases one of the possible TSs has symmetry and calculations can therefore be carried out much more quickly for it than for any of the others. Naturally this is the one that is studied first.



In view of the importance of our conclusion, we carried out calculations (39) for the enforced boat Cope rearrangements of semibullvalene (3), barbaralane (4), and bullvalene (5), all of which are expected to take place very much more easily by the ARO route because of the effect of ring strain. In each case, formation of the ARO TS involves partial opening of the three-membered ring in the reactant whereas the BR route involves partial formation of an additional three-membered ring. BR TSs were nevertheless found for 3 and 5, even though they were higher in energy by 12.5 and 15.9 kcal/mol, respectively, than the corresponding ARO



TSs.

We were also able to explain (43) the apparently anomalous SDKIEs that had been reported by Gajewski for the Cope rearrangement of 3,3-dicyano-1,3-hexadiene (6). AM1 calculations again predicted the reaction to take place by alternative ARO and BR paths, each with a distinct TS. Here, however, the ARO rearrangement was predicted to be the more facile and the calculated SDKIEs agreed with experiment.

One of our major problems has been the readiness of journals to publish papers "refuting" our procedures on the basis of inadequate *ab initio* calculations. The Cope rearrangement of 1 is a good example. As noted above, this has been claimed to follow the ARO path on the basis of calculations using an inadequate basis set (3-21G). Furthermore, only the ARO TS was located. No serious attempt was made to find an alternative TS.

We therefore decided to investigate the situation further, using the CRAY X-MP/24 computer at the University of Texas Center for High Level Computing. Calculations were carried out (33) at the 3-21G and MP2/3-21G levels. The ARO TS was optimized completely in each case. At these levels there was no BR TS. Its energy was estimated by using the lengths calculated for the forming ( $C_1C_6$ ) and breaking ( $C_3C_4$ ) bonds and optimizing everything else. Single point calculations were then carried out up to and including the MP4/6-31G<sup>\*</sup> level. The difference in energy between the TSs was 25 kcal/mol at the 3-21G level but dropped steadily, being 2.5 kcal/mol at the MP2/3-21G//MP2/6-31G<sup>\*</sup> level. It seems likely that a complete geometry optimization at the MP2/6-31G<sup>\*</sup> would lead to a still smaller difference, if not an inversion, and that inversion would

certainly occur if a still larger basis set were used. We did not attempt this because we had already used over 200 hours of time on the CRAY (worth several hundred thousand dollars at commercial rates) and because we felt we had made our point, i.e. that *ab initio* calculations of this kind must be carried out using a very large basis set and with allowance for correlation if the results are to be chemically significant and that calculations must be carried out for all the possible TSs.

(b) Diels-Alder Reaction. A detailed AM1 study (20) of the Diels-Alder reactions of ethylene, acrylonitrile, and the dicyanoethylenes with 1,3-butadiene suggested that none of these reactions, other than possibly that of ethylene, take place by the conventional "allowed" pericyclic path via an aromatic TS. This conclusion was based on the results of RHF calculations for the "allowed" reactions. It was, however, weakened by the unsatisfactory results obtained for the alternative biradicaloid mechanisms, due to the unreliability of open shell versions of AM1. We suggested, on the basis of our results for the Cope rearrangement (see above), and qualitative arguments concerning the Diels-Alder reaction, that the latter may also take place by either of two alternative routes, with distinct TSs, one involving a very unsymmetrical biradicaloid (BR) TS and the other a symmetrical aromatic (ARO) one. This suggestion has recently been confirmed by a spectacular *ab initio* calculation by Bernardi *et al.* in which *both* TSs were located for the ethylene-butadiene reaction. The aromatic TS was lower in energy but only by 2 kcal/mol. Since most substituents would be expected to stabilize the BR TS more strongly than the ARO, it seems clear that reactions involving unsymmetrical reactants must in general take place by the BR mechanism.

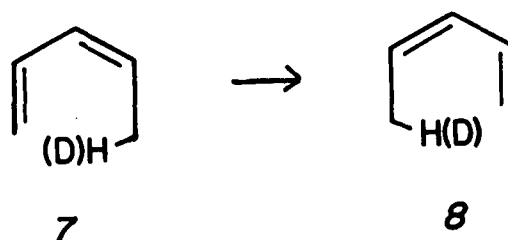
(c) Claisen Rearrangement. A MNDO study (44) of the Claisen rearrangements of a number of allyl vinyl ethers suggested that they follow a BR mechanism similar to that of the formally analogous Cope rearrangements. This conclusion has, however, been revised somewhat in the light of a subsequent detailed AM1 study (31). The reactions are indeed similar, as would have been expected. However, since the Claisen rearrangement is inherently strongly exothermic, its TS is an "early" one where the distinction between the ARO and BR paths is correspondingly less distinct. The TSs therefore vary in structure between the two extremes, rather than falling into two distinct groups.

(d) Dipolar Additions. Extensive AM1 calculations have been carried out for dipolar addition reactions of fulminic acid (56), nitrile oxides (57), and nitrones (58) with various dipolarophiles. The results suggest very strongly that the reactions are not normal ARO-type pericyclic processes but involve biradicaloid or zwitterionoid species as intermediates or TSs. As in the case of Diels-Alder reactions, the regioselectivity of dipolar reactions can be understood easily on this basis.

(e) 'Ene Reaction. Extensive AM1 calculations have been carried out for a number of 'ene reactions (50). Our earlier results suggested that these take place by a concerted ARO mechanism involving an aromatic TS. While the calculated activation energies were too large by an unusually large amount, the error seemed to be systematic and the TSs showed no signs of biradical character. Later BIRADICAL calculations suggest, however, that the reactions may in fact take place in a nonsynchronous manner, via biradical-like species as intermediates or TSs. The

distinction cannot be made on the basis of kinetic isotope effects because the values calculated for both mechanisms agree with one another and with experiment.

(f) 1,5-Sigmatropic Rearrangement of 1,4-Pentadiene. We had previously suggested that the 1,5-sigmatropic hydrogen shift in 1,4-pentadiene (7  $\rightarrow$  8) involves tunnelling from vibrationally excited states (vibrationally excited tunnelling, VAT) because the observed deuterium kinetic isotope effect ( $\sim 5$ ) was too large to be accounted for otherwise. This conclusion was supported by the AM1 calculations noted in the previous paragraph, the deuterium kinetic isotope effect calculated for (7  $\rightarrow$  8) being similar to those ( $\sim 2.5$ ) calculated, and observed, for various 'ene reactions.



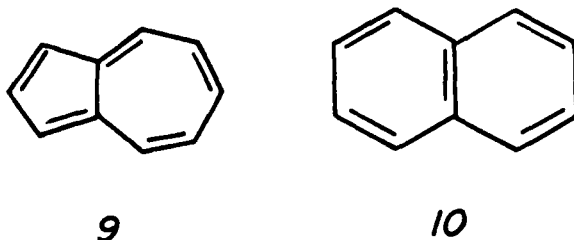
This conclusion has been challenged by Houk *et al* on the basis of 3-21G *ab initio* calculations which led to a good estimate of the activation energy. The calculated deuterium kinetic isotope effect agreed with our values and with those calculated and observed for the 'ene

reactions noted above, as Houk *et al* themselves pointed out. They suggested that the discrepancy might be due to their use of an uncorrelated wave function. Since it seemed to us unlikely that correlation could have such an effect, we calculated the kinetic isotope effect at the MP2/3-21G level (38). As expected, the result agreed almost exactly with the RHF/3-21G value quoted by Houk *et al.*, which we also reproduced. These results seem to leave little doubt that VAT is indeed important in the rearrangement of 12.

(g) Elimination Reactions. A very extensive study (59) of nucleophilic elimination (E2) reactions has provided a consistent picture of the way their rates depend on structure, the calculations referring of course to the gas phase. The mechanisms seem to show a more or less continuous transition from ones close to the E1 extreme at one end to ones close to the E1cb extreme at the other.

Alkyl substituents are known to exert different effects on eliminations involving neutral leaving groups (e.g. halogen) and charged ones ('onium ions); cf. Saytzeff's rule with Hoffman's rule. This difference was correctly reproduced by AM1, but for reasons that differ from those commonly assumed. Thus the halide eliminations corresponded to E1cb-like TSs, involving primarily breaking of the CH bond while the TSs for elimination from 'onium ions were E1-like, corresponding to heterolysis of the leaving group. Current interpretations assume that the former are genuine more-or-less-synchronous E2 reactions, the latter being E1cb-like. It will be interesting to see whether the discrepancy can be attributed to solvent effects.

(h) The Azulene-to Naphthalene Rearrangement and the Automerization of Naphthalene. Azulene (9) rearranges cleanly to naphthalene (10) at high temperatures. The mechanism of this remarkable reaction has not been established. Similar comments apply to the thermal scrambling of the carbon skeleton in naphthalene, an even more remarkable reaction which has been detected by isotopic labelling and which also takes place without significant formation of byproducts, even though it requires a temperature close to 1000 K.



We carried out a very extensive MNDO survey (3,17,18) of the relevant parts of the  $C_{10}H_8$  potential surface, locating 89 stationary points corresponding to stable species and the transition states for their interconversions. This is certainly the most extensive calculation that has been reported for any system, using any quantum chemical procedure. The reactions had moreover to be studied by open shell procedures because they involved biradical-like intermediates and, to make things worse, the UHF approximation proved inadequate. We therefore had to use the BIRADICAL

option (half-electron method + 3x3 CI) at a time when derivatives of the energy still had to be found by finite difference; see Section 2.2(a) above. Our calculations provided strong evidence for a modification of one of the mechanisms that had been suggested and this seems to have been accepted by the experimentalists involved.

(i) The Reformatsky Reaction. MNDO calculations for the Reformatsky reaction between methyl bromoacetate and formaldehyde provided strong evidence for a new mechanism, involving a metallo-Claisen rearrangement of an enolized form of a dimeric adduct formed by the reactants (30).

(j) Formation of Soot. It has been suggested that a key step in the formation of soot from benzene is ring opening of phenyl radical to form a highly unsaturated open chain radical. The activation parameters calculated (28) for this reaction, using AM1, led to a rate constant in remarkable agreement with an experimental estimate, providing strong support for the postulated mechanism.

(k) A Phenomenally Large Secondary Deuterium Kinetic Isotope Effect. A phenomenally large (-2) SDKIE has been observed in the conversion of *trans*-1-phenylcyclohexene to the normal *cis* isomer. Our AM1 calculations (31) led to a reasonable estimate of the activation barrier and the SDKIE, confirming the experimental result. The calculations also accounted for the large SDKIE, formation of the TS involving an exceptionally large displacement of the relevant H(D) atom.

(l) Substitution at Carbonyl Carbon. During the previous contract period we found that addition of anionic nucleophiles to carbonyl carbon, and analogous substitution reactions at carbonyl carbon, take place without activation in the gas phase. Our conclusions, based on MNDO and AM1 calculations, have been confirmed by subsequent *ab initio* ones. Only a few reactions were reported in our original communication. A full account of our work has now been submitted for publication (47).

(m) Reactions of Stannanes with Bromine. A detailed MNDO study (12) of the reaction of bromine with tetramethylstannane seems to have explained some puzzling experimental results.

(n) Wittig Reaction. Calculations have been carried out (60) for the Wittig reactions of the ylides  $\text{Me}_3\text{P}=\text{CH}_2$  and  $\text{Me}_3\text{P}=\text{CHCH}_3$ , derived from tetramethylphosphonium ion and ethyltrimethylphosphonium ion, respectively, with formaldehyde, acetaldehyde, and benzaldehyde. The reactants are predicted to combine directly to form the phosphaoxetane as a stable intermediate, without any indication of formation of an intermediate zwitterion. The predicted products agreed with rules based on experiment and analogous reactions of other phosphorus ylides.

### 3.2 Enzyme Reactions.

During the previous contract period, the work referred to in the previous paragraph led us to propose a novel explanation for the high activity and selectivity of enzymes as catalysts. A further account has now been published (21). Calculations for two specific enzyme reactions, which support our theory, are summarized below.



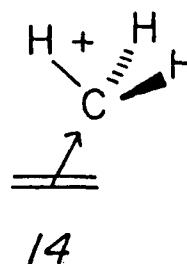
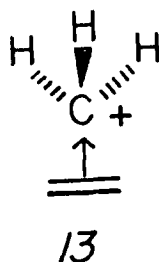
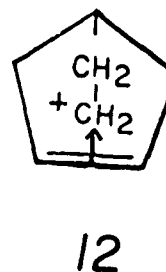
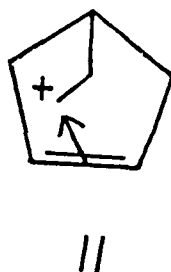
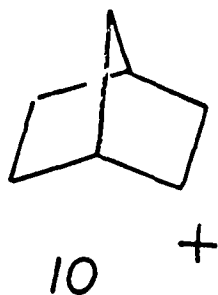
(a) Enzymatic Synthesis of Squalene from Farnesyl Pyrophosphate. This reaction is the key step in the biosynthesis of steroids and therefore of major biological importance. We studied its mechanism by calculations (24) for a series of appropriate models. The results provided strong support for a mechanism which differs in several respects from those previously suggested and in which the exclusion of water from between the enzyme and substrate plays a key role. The calculations also led to suggestions concerning the structure of the active site.

(b) Mechanism of Chain Extension in the Biosynthesis of Fatty Acids. AM1 calculations (40) for reactions of model systems seem to have clarified the mechanism of the chain extension step in the synthesis of fatty acids by fatty acid synthetase. The results again emphasized the role of dehydration and the potential value of AM1 as a tool for studying enzyme mechanisms.

#### 4. OTHER APPLICATIONS

(a) Proton Affinities and Deprotonation Energies. AM1 calculations have been carried out (22) for the proton affinities and deprotonation energies of virtually all the compounds for which reliable experimental data and AM1 parameters were available. The results agreed well with experiment, better indeed than those given by any but "state of the art" *ab initio* procedures. This work has aroused much interest among biochemists and theoreticians concerned with the mechanisms of enzyme reactions.

(b) Structure of Corner Protonated Cyclopropane and the 2-Norbornyl Cation Problem. We have pointed out (10,19) that the available experimental evidence concerning the notorious 2-norbornyl cation (10) shows it to be nonclassical but at the same time not symmetrical. This suggests that it is best formulated as an unsymmetrical  $\pi$  complex, 11. While high level *ab initio* calculations have been carried out for the symmetrical structure (12), it was not identified as a minimum on the potential energy surface and no effective attempt was made to find an alternative unsymmetrical structure. According to our interpretation, the symmetrical structure is a saddle point, being the TS for interconversion of two unsymmetrical  $\pi$  complexes.



It was, however, difficult to see why the ion should be unsymmetrical if the parent ion is symmetrical, i.e. 13, as has been generally assumed and as was implied in a much quoted high level *ab initio* study by Pople, Schleyer, et al. Careful examination of their paper showed, however, that the symmetrical species was not shown to be, or even specifically claimed to be, a minimum on the corresponding potential energy surface. We have now repeated (25) the calculations in more detail, characterizing 17 by calculating force constants. It is not a minimum. It is a saddle point, being indeed the TS for interconversion of two mirror image unsymmetrical  $\pi$  complexes, 14. This remained true even at higher levels of *ab initio* theory. This work removes the last objection to our formulation of 2-norbornyl cation as an unsymmetrical  $\pi$  complex.

(c) Testing *Ab Initio* Procedures. One of our problems has been to substantiate claims that our procedures are comparable with reasonably good *ab initio* ones because of the lack of objective tests of the latter. The errors in the *ab initio* energies for atoms and molecules are enormous and the same is true of heats of formation derived from them. Any use of *ab initio* methods in chemistry must depend on cancellation of errors in calculating heats of reaction or activation and no systematic studies of these have been carried out.

We pointed out a solution of this problem some years ago. If a method reproduces heats of reaction accurately, it must be possible to assign fixed energies to individual atoms such that their use in conjunction with *ab initio* energies for molecules will lead to accurate heats of formation for the latter. If the atomic energies are determined by a least squares fit to the energies calculated by a given procedure, the errors in the

heats of formation for individual molecules will then indicate the effective errors in the energies calculated for them. We have now developed (27) an improved procedure for finding the atomic energies and applied it to the 3-21G and 6-31G\* models, using additional *ab initio* data that have become available recently. Since an IBM PC version of the program has been deposited with QCPE, there is now no excuse for the use of untested basis sets in *ab initio* calculations. It will be interesting to see if our contribution has any effect on this unfortunate practice.

#### OTHER PUBLICATIONS

A number of other papers were published during the early part of the Contract period, describing work carried out during the previous period. Since the work in question was reviewed in the corresponding Final Report, it is not discussed here.

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- (2) On the Double Proton Shift in Azophenine (Michael J. S. Dewar and Kenneth M. Merz, Jr.) TheoChem 124, (1985) 183.
- (3) Mechanisms of the Azulene to Naphthalene Rearrangement (Michael J. S. Dewar and Kenneth M. Merz, Jr.) J. Am. Chem. Soc., 107, (1985) 6111.
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- (5) Stannylenes: An MNDO Investigation (Michael J. S. Dewar, James E. Friedheim, and Gilbert L. Grady) Organometallics 4, (1985) 1784.
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- (7) Aspects of Organomercury Chemistry (Michael J. S. Dewar and Kenneth M. Merz, Jr.) Organometallics 4, (1985) 1967.
- (8) MNDO Calculations for Compounds Containing Lead (Michael J. S. Dewar, Mary K. Holloway, Gilbert L. Grady, and James J. P. Stewart) Organometallics 4, (1985) 1973.
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(27) Testing Ab Initio Procedures; the 6-31G\* Model (Michael J. S. Dewar and Brendan M. O'Connor) Chem. Phys. Lett. 138, (1987) 141-145.

(28) Rate Constant for Cyclization/Decyclization of Phenyl Radical (Michael J. S. Dewar, W. C. Gardiner, Jr., M. Frenklach, and I. Oref) J. Am. Chem. Soc. 109, (1987) 4456-4457.

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(30) The Reformatsky Reaction (Michael J. S. Dewar and Kenneth M. Merz, Jr.) J. Am. Chem. Soc. 109, (1987) 6553-6554.

(31) An Unusually Large Secondary Deuterium Isotope Effect. Thermal Trans-Cis Isomerization of trans-1-Phenylcyclohexene (Richard A. Caldwell, Hiroaki Misawa, Eamonn F. Healy, and Michael J. S. Dewar) J. Am. Chem. Soc. 109, (1987) 6869-6870.

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(34) A New Mechanism for Superconductivity (Michael J. S. Dewar) Angewandte Chemie 26/12, (1987) 1273-1275.

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(43) "Cope Rearrangement of 3,3-Dicyano-1,5-Hexadiene; Duality of Mechanism in Pericyclic Reactions". M.J. S. Dewar, C. Jie. Chem.Comm.

(44) "Mechanism of the Claisen Rearrangement of Allyl Vinyl Ethers" M. J. S. Dewar, C. Jie. JACS



(45) "DEWAR-PI Study of Electrophilic Substitution in Selected Polycyclic Fluoranthene Hydrocarbons". M. J. S. Dewar, R. D. Dennington. JACS

(46) "Aromatic Energies of Some Heteroaromatic Molecules" M. J. S. Dewar and A. J. Holder. Heterocycles

#### MANUSCRIPTS IN COURSE OF PUBLICATION

(47) "Anionic Substitution at Carbonyl Carbon. Implications for the Chemistry of Ions in Solution". M. J. S. Dewar, D. M. Storch. Sent to Perkin Elmer - 6-15-88.

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(49) "AM1 Parameters for Phosphorus", M. J. S. Dewar, C. Jie. Submitted 2-22-88. THEOCHEM

(50) "Mechanism of the Alder (Ene) Reaction", M. J. S. Dewar, C. Jie.

(51) "Is Triquinacene Homoaromatic?; A Computational Study" M. J. S. Dewar and A. J. Holder.

#### MANUSCRIPTS TO BE SUBMITTED

(52) "AM1 Parameters for Sulfur" M. J. S. Dewar, Yate-Ching Yuan.

(53) "AM1 Parameters for Germanium" M. J. S. Dewar, C. Jie.

(54) "AM1 Parameters for Mercury" M. J. S. Dewar, C. Jie.

(55) "A New Method for Locating Transition States" M. J. S. Dewar, D. Liotard.

(56) "Dipolar Addition Reactions of Fulminic Acid" M. J. S. Dewar, R. D. Dennington.

(57) "Dipolar Addition Reactions of Benzonitrile Oxide" M. J. S. Dewar, R. D. Dennington

(58) "1,3-Dipolar Cycloadditions of Nitrones" M. J. S. Dewar, R. D. Dennington.

(59) "Nucleophilic Elimination Reactions" M. J. S. Dewar, Y-C Yuan.

(60) "Mechanism of the Wittig Reaction" M. J. S. Dewar, A. Pierini.